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J. G. Stoll, Jr.

Ralph E. White
University of South Carolina - Columbia, white@cec.sc.edu

J. J. Ehrhardt

R. I. Masel

J. P. Merrill

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Scattering of light atoms from strongly periodic surfaces

A. G. Stoll Jr.*, R. E. White, J. J. Ehrhardt†, R. I. Masel, and R. P. Merrill

Department of Chemical Engineering, University of California, Berkeley, California 94720

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Atomic scattering from weakly periodic metal surfaces exhibits no diffraction, but the phenomenological effects of strong inelastic transitions is clearly evident, particularly for the larger, more polarizable rare gases. Strongly periodic surfaces like LiF display resolved He diffraction and rainbow scattering of Ne for thermal beams. The W(112) surface, perpendicular to its close-packed ridges, shows both diffraction of He and rainbow scattering of Ne. Semiclassical trajectory calculations reproduce these results for He scattering from metal surfaces, indicating the absence of any structured scattering along nearly close-packed rows. The calculations indicate that the effective scattering cross sections are larger than those based on crystal radii and predict diffraction maxima at energies of $2k T_g$ and the observed relative intensities. Simple Debye–Waller analysis appears to describe thermal attenuation of diffraction maxima, and the mean square displacements are equal to those based on electron scattering. Helium diffraction is sensitive to the presence of ordered adsorbed layers, but quantitative interpretation of the surface structures is yet to be worked out.

INTRODUCTION

There has been a great deal of experimental activity in recent years on the scattering of well-collimated beams of the rare gases and simple molecules from solid surfaces.[1] Furthermore, a good deal of work in the past five years has been carried out on surfaces whose structure and composition could be verified *in situ* or inferred from comparison with data taken on surfaces the same as or similar to those whose structure and composition had been verified. The sensitivity of light gas scattering to surface disorder and contamination[2] has been amply demonstrated even to the point that specular helium scattering from simple metal surfaces can be used to monitor adsorption.[3] Until recently only unilobular scattering of helium and neon has been observed from metal surfaces which have been represented primarily by fcc (111),[4] fcc (100),[5] and bcc (110).[6] By contrast, from the earliest days of atomic scattering from surfaces[1] helium has exhibited diffraction from alkali halide surfaces.[8] To date, diffraction has been observed from only two metallic surfaces, WC(3×5) (110)[9] and W(112).[10,11]

A second type of structured scattering has been observed in experiments with thermal neon beams from LiF[12] and more recently from W(112) metal surfaces.[11] This broad bilobular scattering, termed rainbow scattering by McClure,[13] is not observed, however, when monoenergetic neon beams are scattered from LiF,[14] where rather well-resolved diffraction features are observed up to beams of several orders. While McClure's description of the rainbow scattering is based entirely upon classical mechanics, it is clear from William's work[14] that the scattering is, in fact, within the quantum regime. It has become apparent from recent calculations[15,16] based on semiclassical trajectory theory[17] that the classical rainbow plays a central role in determining the intensities of diffracted beams and that when realistic potential surfaces are used, rainbow scattering results from simple energy averaging of the diffraction beams over the energy distribution of the incident beam.[18]

The purpose of this paper is to review the scattering of light atoms and molecules from strongly periodic surfaces and present a short overview of recent work in this laboratory on the scattering of helium and neon from W(112) surfaces. More detailed presentations of these results will appear elsewhere.[18–20]

ATOMIC SCATTERING FROM METAL SURFACES WITH WEAK PERIODICITY

The fcc (100), fcc (111), and bcc (110) surfaces are similar in that the centers of all their surface atoms lie in the same plane and if the sizes of the atoms are all identical, such surfaces represent the smoothest possible "hard sphere" surfaces. Since the atomic diameters at thermal energies even of the lightest gases are quite large (2.6 Å for He), the amplitude of the surface periodicity is further reduced. In the case of metals where the valence electrons may be crudely envisioned as an electron fluid with "high-surface tension," the surface periodicity is reduced even more. Typical scattering patterns of the rare gases from such surfaces are shown in Fig. 1. In all cases the scattering distributions are unilobular even though the deBroglie wavelengths associated with the average beam energy (0.639 Å for

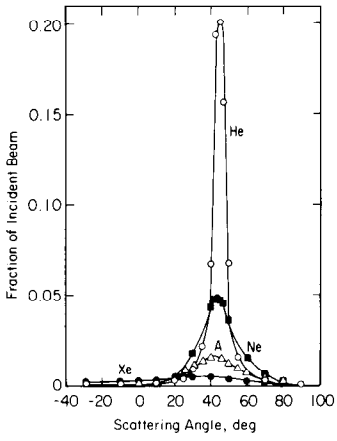

FIG. 1. Rare gas scattering from platinum (111).

He and 0.436 Å for Ne) are such that diffraction features should be resolved for He and Ne if the diffracted beams constitute significant portion of the total scattered flux. On the contrary, integration of the specular He beam has proved to give a mass balance within 5% of the incident beam.[24]

What is evident in the scattering patterns of Fig. 1 is a marked increased in the inelastic interactions as the mass and polarizability of the incident atoms increases. This correlates well with the known values of the heats of adsorption of the rare gases when considering either a series of gases scattered from one metal surface or when considering a single gas scattered from a series of metals. As a result it has been possible to classify the scattering from such surfaces into three phenomenalogical regimes, quasielastic, inelastic, and trapping dominated, depending on the ratio of the average energy of the incident beam to the "well-depth" of the gas-solid potential.[1,21]

That the absence of diffraction from these "smooth" metal surfaces is no experimental artifact is emphasized by the work done concurrently with LEED studies of the surface crystallography[2–5,11,21] and by work of Palmer, *et al.*[22] They showed that experimental procedures which produced diffraction from LiF exhibited no diffraction from an Ag(100) grown epitaxially *in situ* and on-top-of the diffracting LiF.

DIFFRACTION AND RAINBOW SCATTERING FROM LiF

An example of the diffraction of a thermal helium beam from LiF is displayed in Fig. 2. The first order

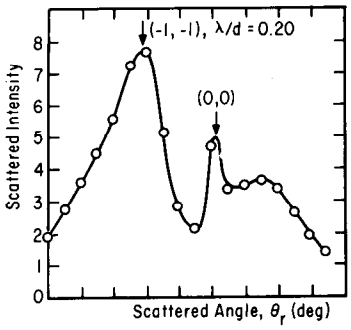

FIG. 2. Diffraction of a thermal (300 K) helium beam from LiF (001).[8]

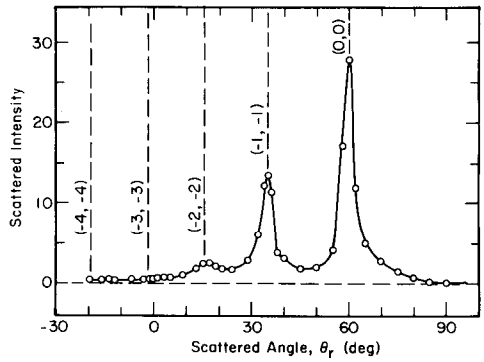

FIG. 3. Diffraction of a monoenergenic helium beam from LiF (001).[8]

diffracted beams are clearly evident and they appear at a wavelength characteristic of the flux-averaged incident beam energy, $2kT_g$, i.e.,

$$\lambda = \frac{h}{2(M_g k T_g)^{\frac{1}{2}}} \tag{1}$$

and

$$\pm(\sin\theta_r - \sin\theta_i) = \frac{J\lambda}{d}, \tag{2}$$

where λ is the deBroglie wavelength, M_g is the mass of gas atom, T_g is the source temperature of the thermal beam, θ_r is the angle of reflection, θ_i is the angle of incidence, J is the diffraction order, an integer, and d is the lattice spacing perpendicular to the incident beam.

The observed width of the diffracted beams is consistent with the dispersion expected in λ from the energy distribution of the incident beam.[23] It is obviously too large to observe the effects of discrete phonon interactions with the thermal surface. In Fig. 3 is shown a helium scattering distribution using a nozzle beam (nearly monoenergetic) from a LiF surface.[8] The angular resolution of Williams' work[8] is also much greater than that of O'Keefe *et al.*[8] The diffraction peaks for the nozzle beam are resolved up to several orders and in the work of Williams[8] several satellite peaks are evident around each diffraction beam, probably resulting from discrete phonon exchange processes. If so, then multiphonon processes are indeed quite probable as Beebe[24] and Drauglis, *et al.*[25] have argued.

Williams has also demonstrated the inherent utility of helium diffraction in the study of adsorbed layers on the solid surface.[26] In view of this sensitivity of the helium to the structure of adsorbed layers it seems only fair to point out that there is some uncertainty about the cleanliness of the LiF surfaces in all of these studies. There is strong evidence[8] to indicate that these surfaces may be covered by at least a monolayer of water.

When thermal Ne beams are scattered from these LiF surfaces, typical rainbow scattering patterns are observed[12] (see Fig. 4). Note that there are two broad prominent peaks, one forward scattered and one backward scattered, with some weak fine structure in be-

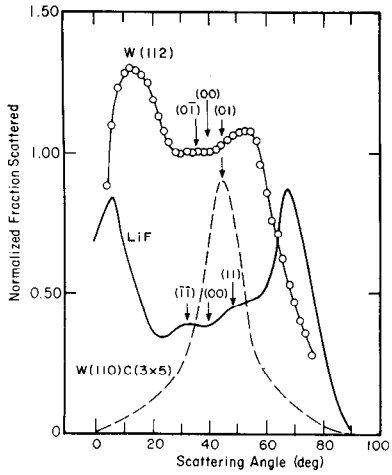

FIG. 4. Comparison of scattering patterns for neon scattered from W(112), LiF(001), and WC(3×5) on W(110).

tween which can apparently be indexed to first order diffraction features. It is interesting to note, however, that the (00) (i.e., specular) beam is a minimum in intensity from this surface while it is the *only* beam present on the weakly periodic metal surfaces (see Fig. 1). Characteristic of this rainbow scattering is that the separation of the rainbow peaks decreases with more grazing angles of incidence, with larger gas molecules, and higher beam temperatures.[12] All of this is consistent with a correlation of the separation between the rainbow peaks with the increase in the effective amplitude of the surface periodicity.

When monoenergetic beams of neon are used[14] scattering distributions like those in Fig. 5 are observed. The individual diffraction beams are clearly resolved and satellite peaks reminiscent of the discrete phonon transitions evident in the helium scattering are also seen though their interpretation is not as straightforward as in the case of the He scattering.

HELIUM AND NEON SCATTERING FROM W(112)

In view of the uncertainty in the composition and structure of the LiF surfaces[8] and the difficulty involved in electron scattering from alkali halides[27] it would be desirable to examine He and Ne scattering from a surface more easily characterized. Because of the extensive empirical information available on the crystallography, composition, and reactivity of tungsten surfaces under a variety of conditions, the announcement of Tendulkar and Stickney[21] that W(112) surfaces give helium diffraction presented the opportunity to study the scattering of light gases from a strongly periodic metal surface whose composition and structure could be established *in situ* in the experimental apparatus in use in our laboratory. Considering the lack of any structured scattering from the weakly periodic metal surfaces, the diffraction from this surface (which consists of a two-dimensional array of close packed atomic ridges) was intrinsically interesting since it only occurred in the principal scattering plane when the incident beam was perpendicular to the ridges[10] and was absent when the incident beam was parallel to the ridges.

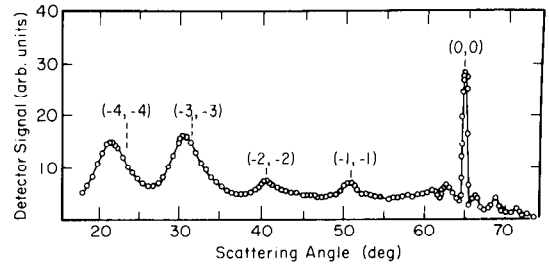

FIG. 5. Scattering of a neon beam from LiF(001).[14]

Using *in situ* LEED and AES measurements it was verified[11] that the diffraction occurred from clean and crystallographically defined W(112). An example of such a diffraction pattern is shown in Fig. 6. Only the first order diffraction features are observed, and the $(\bar{1}0)$ (backscattered) beam is more intense than the (10) (forward scattered) beam. The relative intensity of the first order features increases as the incident beam approaches normal angles and the position of the first-order beams follows the expected Bragg condition [Eq. (2)] even to the exclusion of the (10) beam at approximately grazing angles of incidence.[19]

Neon scattering from the same surface shows rainbow scattering[11] (see Fig. 4) qualitatively very similar to the Ne scattering from LiF. The rainbow peaks are closer together indicating a weaker periodicity for the W(112) surface, a fact strengthened by the observation that argon shows only unilobular scattering from W(112)[20] while some residual rainbow scattering is evident in Ar/LiF.[8] There is also some fine structure between the rainbow peaks, but it is not clear that these features always appear at the same apparent Bragg angle as the temperature of the beam and the angle of incidence are changed. As the beam temperature is increased (see Fig. 7) the rainbow maxima appear to converge and as the angle of incidence increases toward grazing angles the rainbow peaks coalesce so that by an incidence angle of 70° only unilobular scattering is observed.[20] All of this is qualitatively consistent with the results from LiF and with the idea that scattering in

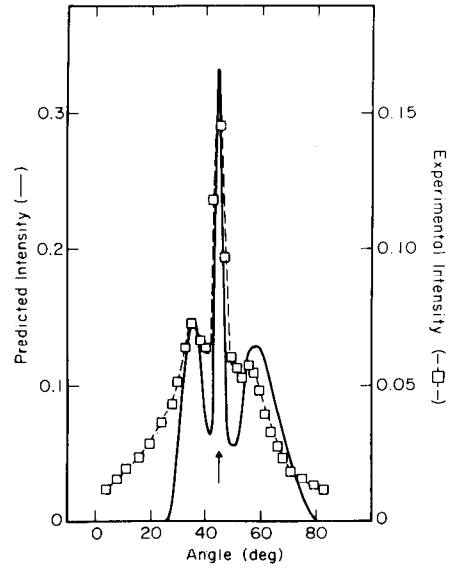

FIG. 6. Comparison of data and semi-classical calculations for helium scattering in the $(1\bar{1}0)$ of W(112).

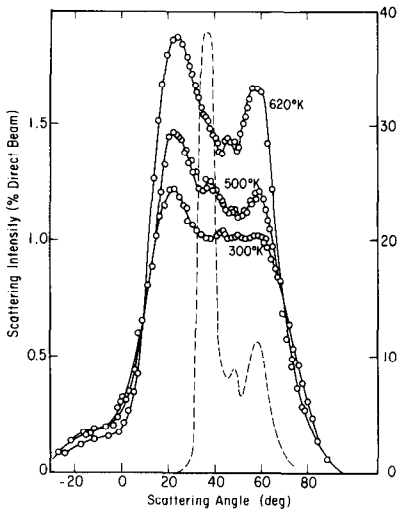

FIG. 7. Scattering of neon from W(112). Experimental with T_s = 1100°C —O—. Semiclassical calculations (– – –).

the quasielastic regime[21] is dominated by the dispersion in local angles of incidence.

SEMICLASSICAL TRAJECTORY CALCULATIONS

In McClure's[13] classical trajectory calculations the rainbow angles appear at extrema in the deflection function (angle of reflection vs impact parameter at a given incident angle and particle energy). The classical result, in fact, gives a singularity in the scattering intensity at the rainbow angle, which can be seen easily from the analytical results of Steele[28] for a simplified surface potential. This singularity is removed from McClure's results when a thermally excited lattice is considered and is entirely replaced by a strong but finite intensity maximum even for a quiescent lattice when the quantum mechanical superposition of the semiclassical theory is properly applied.[29]

In the semiclassical trajectory calculations[15,18] the classical trajectories are calculated as McClure[13] has done to yield the classical deflection function. An example is shown in Fig. 8 for the elastic scattering of He from W(112) perpendicular to the close-packed ridges [i.e., the (1$\bar{1}$0) direction].[18] The essence of the quantum mechanical superposition is that only beams satisfying the diffraction condition [Eq. (2)] are allowed and these beams are phase-shifted by a classical action integral[13,18]

$$\phi = \int_{x_0}^{x} P_x dx + \int P_z dz + P_{x_0} x_0 + P_{z_0} z_0. \qquad (3)$$

Reference to Fig. 8 shows that all of the allowed diffraction beams are composed of two trajectories which are scattered with different impact parameters and, hence, the diffraction amplitude will be proportional to the Jacobian of the classical deflection function modified by the phase interference given by the difference between their action integrals [Eq. (3)]. To represent the diffraction of a thermal beam the entire process must be averaged over the energy distribution of the incident beam. This results in the appearance of the diffraction maxima at approximately $2kT_g$ as observed experimentally rather than at the most probable energy, kT_g, which might have been suggested by intuition.

In Fig. 6 a semiclassical calculation is compared with the experimental results of He from W(112). The calculations give only first order diffracted beams. Higher order beams are either forbidden because they lie outside the classical rainbow angles or modified by such low probabilities in the thermal beam that they do not appear resolved in the averaged distribution. In this connection it should be pointed out that classically forbidden peaks[17] were also calculated but because they are so severely damped, that they also made only a negligible contribution.

A Lennard–Jones, 3–9, potential superimposed upon a surface periodicity deduced from an equivalent hard-sphere model of the surface[18] was used with well depths taken from empirical heats of adsorption. In order to obtain results even qualitatively correct it was necessary to assume an equivalent hard-sphere scattering cross section for the tungsten atoms nearly twice that based on the observed crystal radius of tungsten metal. This is in qualitative agreement with gas-phase scattering results where scattering diameters for diatomic molecules, for instance, are approximately twice the bond distances[30] and van der Wall's radii nearly twice the crystal radii.[31]

In the (11$\bar{1}$) azimuth, which is parallel to the close-packed ridges, the rainbow angles are so close that only the (00) diffraction beam is allowed. This is in agreement with the results of Tendulkar and Stickney[10] and the body of data in existence of the "smooth" metal surfaces.

Similar elastic scattering calculations have been made for Ne/W(112) using a scattering diameter of tungsten equivalent to that used for the helium scattering. These results are shown in Fig. 7 (dashed line). The position of the forwardscattered rainbow peak coincides with the experimental peak in the room temperature distribution, but the backscattered rainbow peak in the calculated distribution is much closer to the specular peak than in the experimental distribution. As with helium, the intensities of the experimental distributions are lower than the calculated ones and significantly broader. Of course it is known from nondiffractive scattering[1,6] that

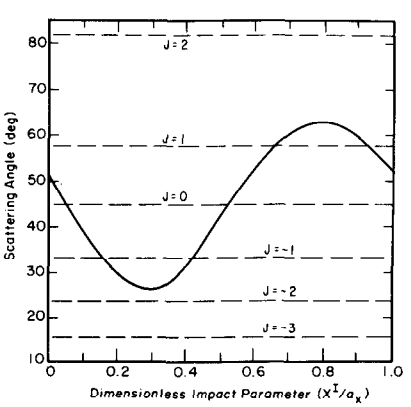

FIG. 8. The classical deflection function for 1.2 Kcal helium scattered in the (1$\bar{1}$0) direction off of tungsten (112).

neon from tungsten is in the inelastic regime, while helium from tungsten is quasielastic. Also, Goodman's perturbation parameter[32] for a distorted wave Born calculation of atomic diffraction would be ca. 0.5 for Ne scattering from tungsten, so it would appear that the inelastic effects must be included in the theory *ab inito*.

The surface temperature for the distribution shown in Fig. 7 is 1100°C and by analogy with the results from close-packed surfaces[1,6] this should result in a net transfer of momentum from the surface to the gas in a direction perpendicular to the surface, resulting in a shift of the backscattered rainbow peak as observed. In fact, an average transfer of about two Debye phonons is all that is needed to shift the calculated backscattered rainbow peak to coincide with the position of the experimental distribution. Of course a fraction of the forward rainbow would also be shifted, but it is unlikely that it would be resolved sharply within the fine structure between the two "rainbow" features.

DEBYE–WALLER ANALYSIS

One striking difference between the semiclassical calculations for helium and the experiments is the relative broadness of the experimental distributions compared to calculated ones. Also, the calculated intensities are twice the experimental ones. The calculations have been performed for a quiescent surface but the experimental surfaces were at finite temperatures and it is well known experimentally that high-surface temperatures attenuate the specular beams in the quasielastic regime.[1–6]

The most direct approach to thermal attenuation in coherent scattering is the so-called Debye–Waller analysis.[33] This approach has been applied by Doll[15] to atomic scattering within the framework of semiclassical theory. The simplest result is that the intensity is attenuated by the usual Debye–Waller factor

$$I/I_0=\exp(-2W), \tag{4}$$

where

$$W=\frac{1}{2\hbar}(\Delta P_x^2\langle u_x^2\rangle+\Delta P_z^2\langle u_z^2\rangle). \tag{5}$$

He points out that if the second term in Eq. (5) dominates that one recovers the usual expression for electron diffraction.[34] If one assumes that the attractive potential acts only normal to the surface then, for the specular beam

$$W=4m\left(\frac{E\cos^2\theta_i+D}{\hbar^2}\langle u_z^2\rangle\right), \tag{6}$$

where: E is the energy of the incident beam and D is the well-depth of the surface potential, which is the result used by Hoinkes *et al.*[35] If D is large compared to E then the result used by Beeby[35] and by Weinberg[36] is obtained. This latter assumption is obviously not appropriate for the thermal scattering discussed here where D/kT_g for He is always less than 0.3. The Debye–Waller analysis even within the semiclassical framework predicts a strong dependence of the thermal attenuation on the incidence angle of a monoenergetic beam. When the Debye–Waller factor is included in the energy averaging, however, the angular dependence for the (00) beam is removed from the exponential

$$\frac{I}{I_0}=\left(1+\frac{8mkT\langle u_z^2\rangle\cos^2\theta_i}{\hbar^2}\right)^{-2}\exp\left(-\frac{8mD\langle u_z^2\rangle}{\hbar^2}\right). \tag{7}$$

The experimental results for diffractive scattering[19] and simple specular scattering[36] of thermal beams are consistant with Eq. (7). For He scattering from W(112) the Debye temperature is 200 K, which agrees with the results from electron scattering.[37]

The Debye–Waller analysis also predicts that the peak intensities should decrease with increasing beam energy and Doll has suggested using this fact to estimate mean-square displacements. The experimental results for close-packed surfaces,[1–6] however, show uniformly that increasing the beam energy increases the specular intensity, while the diffraction of He from W(112)[19] shows an increase in attenuation with beam energy. From the semiclassical point of view there are two effects in addition to Debye–Waller attenuation which must be considered. As the energy increases the beam samples a higher portion of the repulsive surface potential which causes the surface to appear more rough (i.e., so-called structure-scattering[4]) but also the effect of the attractive well on the classical deflection function is attenuated. These have opposite effects on the position of the classical rainbow angles. Within the energy regime represented by the experiments with thermal beams the latter effect dominates and the rainbow angles approach each other at higher beam energies as observed (see Fig. 7). As the rainbow angles approach one another more diffracted beams are attenuated and this tends to increase the specular intensity. This is consistent also with the experimental results of Miller[4] and the calculations of McClure.[13] In view of these additional complications in interpreting inelastic effects it does not appear that it will be possible to extract the mean-square displacements from the intensity as a function of the beam energy as easily as Doll suggests.[15]

There is some doubt as to whether or not the Debye–Waller formalism is, in fact, correct in this semiclassical regime. In He scattering, for example, the residence time in the neighborhood of the surface is long compared to a typical lattice vibration time. A more penetrating study of this and other approaches to account for sur-

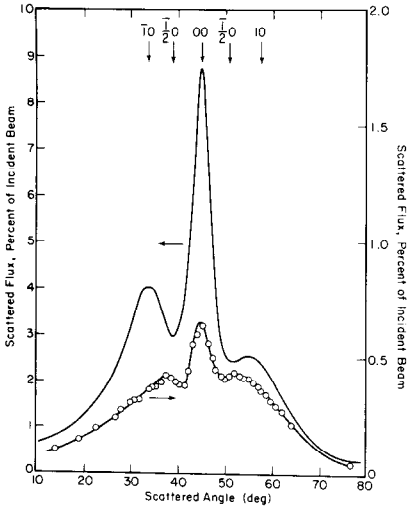

FIG. 9. Scattering of helium in the (110) direction of tungsten (112) covered with a monolayer of oxygen.

face disorder and inelastic interactions is, obviously, in order.

ATOMIC DIFFRACTION FROM ADSORBED OVERLAYERS

The first atomic diffraction pattern ever recorded from a surface, other than the alkali–halides, was observed from a tungsten carbide overlayer on W(110) surfaces.[9] The overlayer (probably metallic WC) had a (3×5) surface lattice and the diffraction was observed perpendicular to the "5" spacing for both He and D_2 even though no diffraction was observed from the clean W(110) surface. No rainbow scattering was evident in the Ne scattering (see Fig. 4), however, the amplitude of the periodicity was probably less than that on the W(112) surface. Nevertheless, because the spacing was so large (five times the W spacing), both first and second order beams were observed for He (i.e., they occurred at angles less than the rainbow angles). Williams[26] has observed diffraction from ordered hydrocarbon layers on LiF and NaF and, as mentioned previously, it is possible that all the scattering from LiF is actually from a monolayer or more of water adsorbed epitaxially upon the LiF surface. In Fig. 9 is shown a He diffraction pattern from a surface of ca. one monolayer of oxygen adsorbed on W(112). It is clear that the strength of the surface periodicity is less for this than it is for the clean metal surface and the inelastic interactions may be somewhat greater.[20] What is of interest here is that small $\frac{1}{2}$ order diffraction beams are discernable and the LEED work from this surface exhibits $\frac{1}{2}$ order beams in the principal scattering plane. It remains to be seen whether or not the semiclassical trajectory calculations can be employed to do structure analysis from such ordered adsorbates on strongly periodic surfaces. The semiclassical analysis makes it clear, however, that the large lattice constants associated with such super-lattices may make them more prominent in the scattering when the periodicity is weak,[9] than the diffraction from the substrate.

Note added in proof: The thermal average of the semiclassical specular beam, Eq. 7, is identical to the form derived by Comsa.[38] From personal communication with H. Wilsch, it would appear that the existence of large amounts of water on LiF surfaces can be ruled out. Experiments using surface ionization mass spectrometry showed no water present on the surface for samples given the standard thermal desorption treatments, but detected large quantities of water when water was allowed to adsorb from the gas phase.

*Present address: Department of Chemical Engineering, California Institute of Technology, Pasadena, California.
†Permanent address: CNRS, Nancy, France.

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